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VOLATILITY CHARACTERISTICS OF MIL-L-7808 TURBINE LUBRICANTS

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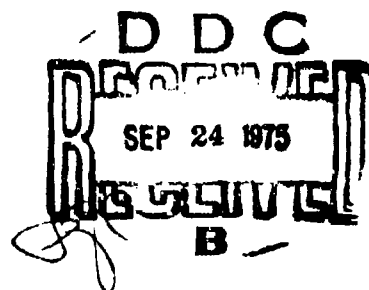
FUELS AND LUBRICATION DIVISION
AIR FORCE AERO-PROPULSION LABORATORY

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AIR FORCE AERO-PROPULSION LABORATORY
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This report contains the results of an effort conducted to investigate the volatility of aircraft turbine lubricants. The work was performed in the Fuels and Lubrication Division of the Air Force Aero-Propulsion Laboratory, Air Force Systems Command, Wright-Patterson AFB, Ohio, under Project 3048, Task 304806 and Work Unit 30480626. The effort was conducted by H. A. Smith/SFL and P. W. Centers/SFL during the period September 1972 to September 1974. Acknowledgment is given to Mr. G. Stambaugh for his outstanding laboratory assistance in test measurement.

This report has been reviewed by the Information Office, (ASD/OIP) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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18. ABSTRACT (Continue on reverse side if necessary and identify by block number) An investigation of MIL-L-7808 lubricant volatility was conducted using ASTM Test Methods D972 and D2878 and by using thermogravimetric analysis. This investigation was conducted to: (1) investigate wide variations in manufacturer's reported batch-to-batch evaporation values which were not supported by gas chromatography; (2) determine evaporation and vapor pressure values of current MIL-L-7808 qualified lubricants using ASTM Test Methods D972 and D2878 and, (3) determine the value of using thermogravimetric analysis for measuring lubricant volatility. <i>over</i>		

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Individual esters, lubricant basestocks and formulated lubricants of known composition were investigated under varying parameters of temperature, gas flow rates and test times. Calibration procedures and check-out of equipment is described.

This investigation has shown that batch-to-batch variation in lubricant volatility does not exist to the extent reported by batch-to-batch quality control testing and that ASTM Method D972 is satisfactory for measuring MIL-L-7808 lubricant evaporation characteristics. Recommendations are given which will enable each laboratory to evaluate test equipment and technique. This investigation has also shown that thermogravimetric analyses does not possess any advantages over ASTM Methods D972 and D2878 for measuring MIL-L-7808 lubricant volatility characteristics.



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INTRODUCTION

Volatility is an important property of aircraft turbine lubricants. Oil consumption, lubricant foaming, pump cavitation and fuel/air/oil cooler efficiency are related to or can be affected by excessive lubricant volatility. However, Squires and Edge (1) contend that some lubricant volatility is desirable for some applications since coking tendency is reduced by increased lubricant volatility.

The defining of acceptable levels of lubricant volatility has been hindered by the inconsistency of volatility data. Volatility is normally evaluated or measured through use of evaporation tests or vapor pressure measurements. Isoteniscope vapor pressure measurements of complex formulated lubricants are not reliable or reproducible and are usually much higher than measurements made by other techniques. Studies made by Beerbower (2) and Coburn (3) show that vapor pressure can be better determined from evaporation loss using ASTM Evaporation Test Method D972-56. Russell, (4) applying this technique to three MIL-L-23699 lubricants, obtained consistent data which was used for calculating lubricant loss during engine operation. (5)

Although the ASTM Evaporation Test Method D972 is relatively simple with respect to technique and equipment, data reported by lubricant suppliers on different production lots of the same formulation varied more than 100% in evaporation values. A similar degree of difference currently exists in evaporation values obtained for the same lubricant by different laboratories. Extensive analysis by gas chromatography has shown that this reported difference in evaporation values cannot be explained by variation in lubricant composition. Therefore, these differences in evaporation test data must be the result of poor test method precision or non-conformance to proper test procedures.

This effort was conducted in an attempt to explain the variations in test results and develop changes in test technique or procedures which will more accurately define lubricant volatility. This investigation covered research in the following areas:

- a. Precision of ASTM Test Method D972 when used for determining volatility of current MIL-L-7808 lubricant formulations.
- b. The actual volatility variations occurring between production batches.
- c. The volatility characteristics of current MIL-L-7808 qualified lubricants using both ASTM D972 and ASTM D2878 procedures.
- d. The value of using thermogravimetric analysis for measuring lubricant volatility.

II

TEST APPARATUS AND PROCEDURE

A. ASTM D 972 EVAPORATION TEST

ASTM D 972-56 test method, "Evaporation loss of Lubricating Grease and Oils (6)", was used for determining the evaporation loss of qualified turbine lubricants, associated basestocks and individual basestock esters. The test apparatus and modifications thereof are as follows.

A Precision Scientific Co. constant temperature bath (Cat. 10193) was fitted with an asbestos fiber-board top having two openings for evaporation test cells. The test cells were firmly fixed to the bath top to maintain a level position. Polyphenyl ether (5P4E) was used for the bath fluid. The volume was adjusted at each temperature to maintain constant fluid height on evaporation test cell.

The standard ASTM test cells were modified by placing a stainless steel O-ring in the groove of the cell cover to eliminate air leakage of the test cells. Both cells were equipped with a thermocouple which was located at the air entry port on the test cell. Also, one cell cover was modified with a tee so that a thermocouple could be lowered just above the lubricant-air interface. The modified cell cover was used to determine temperatures within the cell and was not used for obtaining evaporation test data. Bath temperature was monitored using a mercury thermometer and a thermocouple, and along with air inlet temperature was continuously recorded during each test using a strip chart recorder. Bath temperature was controlled to $\pm 1^\circ\text{F}$ of required test temperature. The temperature variation throughout the bath was less than 1°F at all test temperatures. The bath and associated equipment was installed and operated in a walk-in hood with air flow over the bath controlled. Test procedure outlined by ASTM D 972 was followed except the time of test, test temperature, and gas flow rates were varied as required by the test program. Test equipment utilized for ASTM D 972 measurements was also used for ASTM D 2878 test measurements. Total acid numbers and gas chromatograms were obtained for selected residual evaporation samples which provided information on the nature of evaporation loss and oil degradation loss during the test.

B. THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analyses of the lubricants, basestocks and esters were obtained with a Stone thermobalance Model 5B and a Stone Model LB-202F Recorder-Controller. Special sample cups were fabricated from 0.001 inch thick aluminum foil. Dimensions of the circular, vertical side, flat bottom cups were 0.25 inches in diameter and 0.25 inches in depth.

Thermogravimetric analysis was conducted on 50 to 100 mg of sample under isothermal conditions and at a constant heating rate of 5°C per minute. A flow of 27 ml/min of dry air or nitrogen was introduced into the balance above the sample cup to simulate the gas flow-surface area characteristics of the ASTM D 972 test. Gas was introduced into the hangdown tube so that volatilized or degraded products could be removed without excessive balance vibration. The thermocouple and recorder were calibrated using potentiometric methods and the thermocouple was located as close as possible to the sample cup. For isothermal studies, the sample temperature was controlled to $\pm 1.5^{\circ}\text{C}$ of the desired value. Air and nitrogen flow rates were measured by the soap bubble method. For determinations made under nitrogen, the thermo-balance was evacuated and purged with nitrogen three times prior to test.

III

TEST LUBRICANTS

A total of eighteen lubricant fluids consisting of six MIL-L-7808 formulated lubricants, six basestocks used in these lubricants and six individual esters were studied in this program. Table I presents a listing and description of these materials.

TABLE I

<u>OIL CODE</u>	<u>DESCRIPTION</u>
0-67-11	MIL-L-7808G
0-67-21	MIL-L-7808G
0-67-23	MIL-L-7808G
0-68-7	MIL-L-7808G
0-68-13	MIL-L-7808G
0-70-2	MIL-L-7808G
B-67-21	Basestock for 0-67-21
B-67-23	Basestock for 0-67-23
B-68-7	Basestock for 0-68-7
B-68-13	Basestock for 0-68-13
B-70-2	Basestock for 0-70-2
E-105	Di(2-ethylhexyl) adipate, purity ~ 99%
E-109	Di(2-ethylhexyl) azelate, purity ~ 84%
E-120	2,2-Dimethyltrimethylene nonanoate, purity ~ 89%
E-129	Trimethylolpropane triheptanoate, purity ~ 93%
E-139	Di(2-ethylhexyl) sebacate, purity ~ 97%
E-149	Pentaerythritol tetraheptanoate, purity ~ 93%
E-159	Trimethylolpropane tripelargonate, purity ~ 73%

(Purity determinations made by gas chromatography. Calculations were made using unity detector response for all components.)

Lubricant A	Lot production samples, MIL-L-7808
Lubricant B	Lot production samples, MIL-L-7808
Lubricant C	Lot production samples, MIL-L-7808

IV

TEST RESULTS AND DISCUSSION

A. GENERAL

The subsequent discussion of test results is divided into three sections with each being addressed towards specific goals of the program.

The first section covers the research using ASTM Method D972 and provides data and information relative to test repeatability, batch to batch variations, and effects of test variables including temperature, time and air flow rates on evaporation values. A study was also made to determine the degree of lubricant degradation which occurs in the ASTM D972 test.

The second section covers the research using ASTM Method D2897. Vapor pressure and apparent molecular weights which were calculated from evaporation test data, are given and compared with other reported test data and with calculated theoretical values for known esters. Purity of these esters was established by gas chromatography and is considered in the evaluation of volatility data.

The third section deals with thermogravimetric measurements, correlation with other volatility data, and discusses the value of using thermogravimetric analysis for measuring lubricant volatility.

B. ASTM D972 EVAPORATION TEST DATA

1. Test Precision. Large variations exist in evaporation values currently reported by different laboratories on the same lubricants as shown below.

% Evaporation (ASTM D972, 400°F, 6 1/2 hr)

	Laboratory A	Laboratory B	Laboratory C
Lubricant A	15.3	11.4	9.8
Lubricant B	23.3	19.6	15.1
Lubricant C	14.6	12.8	8.1
Lubricant D	24.3	21.1	15.6
Lubricant E	27.7	14.7	17.1
Lubricant F	14.4	5.0	7.5
Lubricant G	21.8	15.9	9.1

Due to these wide variations, the precision of ASTM D972 was determined by conducting ten tests on lubricant 0-68-13 with the tests being conducted over a three month period. Test conditions were 400°F, 6 1/2 hr test time and 2.583 gm/min air flow. A summary of the test values obtained are given below with individual values given in Appendix A.

Minimum	19.8 % wt
Maximum	22.9 % wt
Mean	21.2 % wt
Standard Deviation	± 1.3 % wt

In addition to these 10 repeat tests, majority of evaporation values obtained for other lubricants, basestocks and esters represent, at least, duplicate determinations. For 90 evaporation values of lubricants, basestocks and esters, conducted at temperatures up to 400°F and gas flow rates up to 3.083 gm/min, over 200 evaporation tests were made. Maximum difference at any one set of conditions was 3.1% with the mean being 0.9%. This precision exceeds that specified by ASTM D972. However, ASTM D972 specifies a 22 hour test under reduced temperatures (210°F to 300°F). At higher temperatures and reduced test times, test precision would be expected to decrease. The data obtained from this study is considered realistic and as such, does not explain the wide range of evaporation values reported by different laboratories.

2. Batch to Batch Variation. Batch to batch variation of evaporation values was investigated using 9 lots of three different formulations. Table II lists the evaporation values reported by the manufacturer while Table III lists evaporation values obtained on the same batches by AFAPL/SFL.

Table II. Manufacturer Batch to Batch Evaporation Values

Manufacturer A:	Lot A	Lot A-1	Lot A-2	Lot A-3
	12.2%	22.8%	19.7%	14.1%
Manufacturer B:	Lot B	Lot B-1	Lot B-2	
	6.6%	11.8%	10.0%	
Manufacturer C:	Lot C	Lot C-1	Lot C-2	
	11.6%	22.6%	29.5%	

Table III. AFAPL/SFL Batch to Batch Evaporation Values

Manufacturer A:	Lot A	Lot A-1	Lot A-2	Lot A-3
	25.3%	25.0%	25.5%	25.6%

Manufacturer B:	Lot B	Lot B-1	Lot B-2
	15.2%	15.1%	15.3%
Manufacturer C:	Lot C	Lot C-1	Lot C-2
	35.5%	34.8%	34.9%

Evaporation values given in Table III support the conclusions made from gas chromatography analyses that batch to batch evaporation values should not vary to the extent shown by manufacturer's quality control data. During the batch to batch testing it became apparent that the two test cell assemblies gave results which varied by about 1.5%. This difference is shown by Table IV.

TABLE IV
Variation of Evaporation Due to Test Assemblies
(Values in % Weight)

Lubricant	A		B		C	
	Cell #1	Cell #2	Cell #1	Cell #2	Cell #1	Cell #2
	26.4	24.2	15.6	14.7	36.8	34.2
	25.3	24.6	15.7	14.5	35.8	33.8
	26.6	24.4	15.6	14.9		
	26.6	24.5				
Mean	26.2	24.5	15.6	14.7	36.3	34.0

Due to above data, careful examination was made of the test bath temperature uniformity, air flow rates and air temperatures, test cell measurements and depth inserted in bath, oil cup dimensions and cell cover dimensions. No differences could be found which would explain the differences shown by Table IV. A series of evaporation tests were then conducted to isolate the test assembly component causing this difference by systematically changing test assembly components. Results of this study are as follows:

	Cell 1	Cell 2
Test Assembly 1 & 2 complete (as received from manufacturer)	26.6 % wt 26.7 % wt	24.6 % wt 24.3 % wt
Oil cup and Cell Cover reversed	25.1 % wt 25.4 % wt 25.0 % wt	25.2 % wt 25.3 % wt 25.3 % wt
Cup only reversed	26.6 % wt 26.5 % wt	25.3 % wt 25.3 % wt
Cell Cover Only Reversed	25.4 % wt 25.0 % wt	25.3 % wt 25.3 % wt

From above data, it is apparent that by changing the test cell lid, variations in evaporation data were minimized. No explanation for the improvement can be offered currently. However, this indicates that the test precision is much better than that obtained in Section B since that data was obtained on test assemblies, 1 and 2, as received from manufacturer and both being used for obtaining evaporation values on each oil.

C. ASTM D-2878 Volatility Test Data.

ASTM method D 2878, "Estimating Apparent Vapor Pressures and Molecular Weights of Lubricating Oils" was investigated using MIL-L-7808 lubricants of known composition, basestock blends and commercial esters used in current lubricant formulations. The theory of this method which is well described by Coburn (3) assumes that Dalton's law of partial pressures applies and that the vapor behaves ideally. Under these conditions, the evaporation test cell assembly would have a Saturation Efficiency factor (SE) given by the following equation:

$$\text{Saturation Efficiency Factor} = \frac{P \times W}{V \times P \times M} \times 22.41$$

where: P (mm Hg) = test cell pressure (760 mm Hg for this report)

W (gm) = grams of material evaporated

V (l) = volume of gas plus vapor at standard conditions (0°C, 760 mm Hg)

P (mm Hg) = vapor pressure of material

M = molecular weight of material

The saturation efficiency was determined at three temperatures using m - terphenyl. The advantages of using this material as a calibration standard are good stability, availability, and volatility characteristics. One disadvantage of this material is its melting point of about 90°C. Vapor pressure values for m - terphenyl, obtained from the literature (8), were used for obtaining the following equation relating the vapor pressure of m - terphenyl with temperature. Using the equation

$$\log P = 8.25175 - 3446.38 \left(\frac{1}{T} \right)$$

where P = mm Hg

T = Temperature in degrees Kelvin

the vapor pressure of m - terphenyl is .32 mm Hg at 250°F, 1.22 mm Hg at 300°F and 10.85 mm Hg at 400°F. Calculated SE factors are as follows:

Temperature	wt. loss, g	Calculated SE Factor	ASTM D2878 SE Factor
121.11°C (250°F)	0.291	0.02591	0.02247
148.89°C (300°F)	0.493	0.03831	0.04204
204.44°C (400°F)	6.687	0.05843	0.06483

Since ASTM D2878 requires that the evaporation loss of m - terphenyl at 300°F, 1/2 hours, 2.583 g per min air flow be 0.503 ± 0.05 grams as compared to 0.493 shown above, the difference in the SE factors is apparently due to differences in the vapor pressure values used for the m - terphenyl. Vapor pressure values of 1.13 and 9.78 at 300°F and 400°F respectively would give calculated SE factors equal to those given in ASTM D-2878.

Vapor pressures of materials studied, calculated using the following factors, are given in Table V.

Temperature	SE Factor
176.67°C (350°F)	0.05020
196.11°C (385°F)	0.05577
204.44°C (400°F)	0.05843
212.78°C (415°F)	0.06103

Individual test data and associated test conditions are given in Appendix A.

TABLE V
VAPOR PRESSURE CALCULATED
FROM EVAPORATION DATA
(2.583 g/min AIR BLOW)

OIL CODE	(1) MOLECULAR WEIGHT	TEST TEMP. °F	5% WT. EVAP. DATA		6 1/2 HR. EVAP. DATA	
			V.P. (mm Hg)	(2) CALCULATED M.W.	V.P. (mm Hg)	(2) CALCULATED M.W.
0-67-11	426	350			0.88	
		385			1.92	
		400	2.34	372	2.59	364
0-67-21	415	350			1.17	
		385			1.97	
		400	3.22	349	2.46	370
		415			2.84	
B-67-21	421	400	3.30	347	2.70	361
0-67-23	435	350			0.68	
		385			1.53	
		400	2.01	382	2.10	378
		415			2.63	
B-67-23	422	400	1.92	388	2.36	372
0-68-7	436	350			0.31	
		385			0.79	
		400	1.01	394	1.16	384
		415			1.57	
B-68-7	441	400	1.16	383	1.71	356

TABLE V (Cont.)
VAPOR PRESSURE CALCULATED
FROM EVAPORATION DATA

OIL CODE	(1) MOLECULAR WEIGHT	TEST TEMP. °F	5% WT. EVAP. DATA		6 1/2 HR. EVAP. DATA	
			V.P. (mm Hg)	(2) CALCULATED M.W.	V.P. (mm Hg)	(2) CALCULATED M.W.
O-68-13	434	350	0.58			
		385			1.33	
		400	1.81	390	1.82	390
		415			2.36	
B-68-13	434	400	1.62	400	2.19	375
O-70-2	389	350			0.94	
		385			2.26	
		400	2.72	334	3.19	324
		415			3.99	
B-70-2	383	400	3.08	327	3.84	313
E-105	371	400	3.73	317		
		400	(3)3.70	317		
E-109	413	400	1.96	351	2.04	348
E-109	413	400	(3)1.74	364		
E-120	384	400	2.62	337		
E-120	384	400	2.91	330		
E-129	470	400	0.72	464	0.87	446
E-129	470	400	(3)0.67	472		

TABLE V (Cont.)
VAPOR PRESSURE CALCULATED
FROM EVAPORATION DATA

OIL CODE	(1) MOLECULAR WEIGHT	TEST TEMP °F	5% WT. EVAP. DATA		6 1/2 HR. EVAP. DATA	
			V.P. (mm Hg)	(2) CALCULATED M.W.	V.P. (mm Hg)	(2) CALCULATED M.W.
E-139	427	400	1.45	369		
E-149	584	400	0.24	555	0.24	555
E-149	584	400	(3)0.08	706		
E-159	554	400	0.28	545	0.28	545
E-159	554	400	(3)0.12	645		

(1) Apparent Molecular Weight Calculated from Formulation Data for the Oils and Basestock Materials.

(2) Molecular Weight Calculated from ASTM D-2878.

(3) Nitrogen Flow Rate of 2.583 g/min.

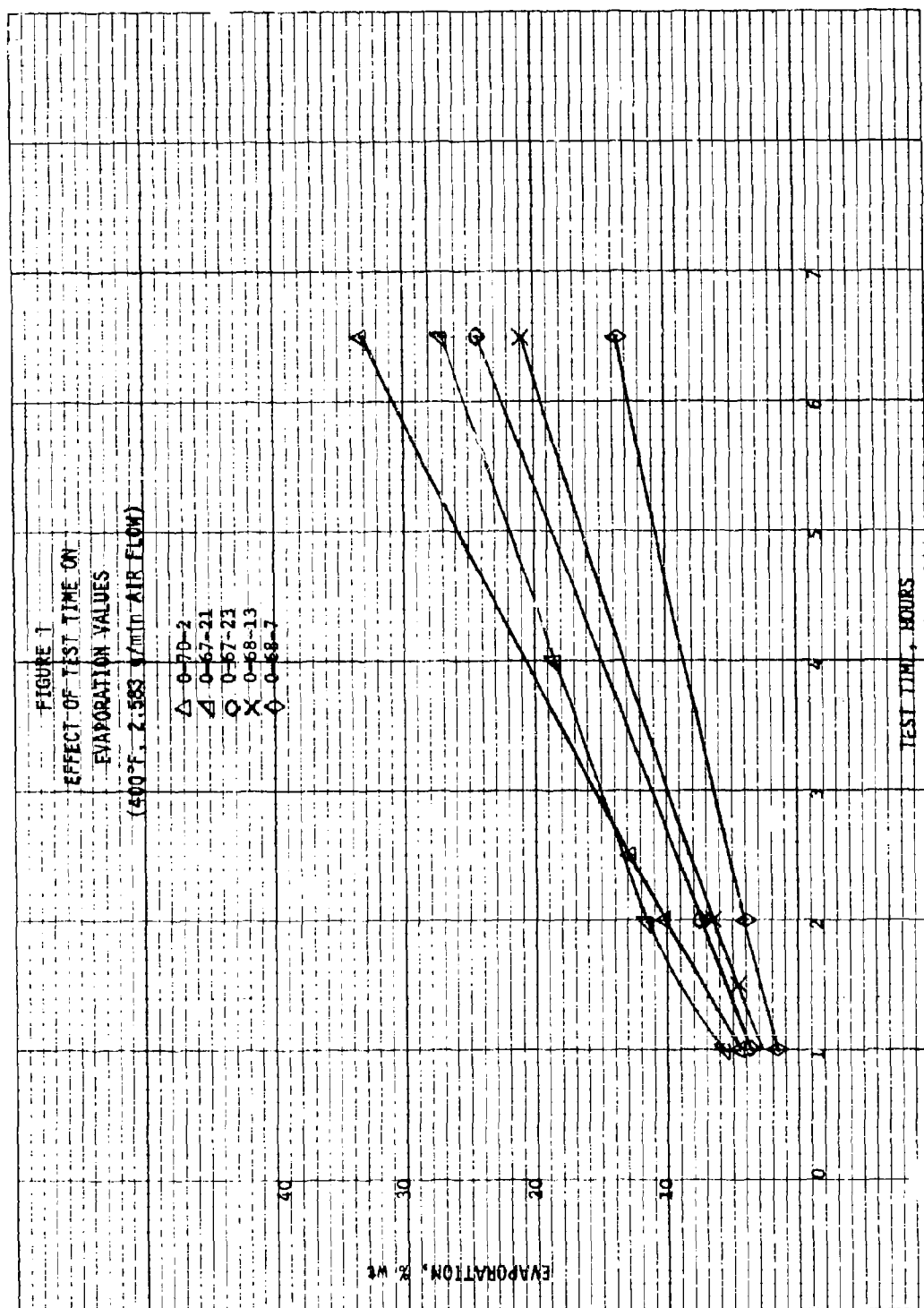
TABLE VI
THEORETICAL VERSUS CALCULATED MOLECULAR
WEIGHTS FOR MIL-L-7808 LUBRICANTS

OIL CODE	MOLECULAR WEIGHT (1)	MOLECULAR WEIGHT SFL		MOLECULAR WEIGHT
	THEORETICAL	(2)	(3)	(4) ASTM D2878
0-67-11	426	392	384	372
0-67-21	415	366	388	349
B-67-21	421	365	381	347
0-67-23	435	404	401	382
B-67-23	422	408	392	388
0-68-7	436	460	449	394
B-68-7	441	449	417	383
0-68-13	434	413	412	390
B-68-13	434	422	398	400
0-70-2	389	380	367	334
B-70-2	383	370	352	327

- (1) Apparent molecular weight calculated from formulation data.
- (2) Calculated from $\text{Log } p = 2.48318 - 0.00539M$ derived from p versus molecular weight curve for known esters. 5% wt loss evaporation data.
- (3) Same as (2) but using 6 1/2 hour evaporation data.
- (4) Calculated according to ASTM D 2878.

For all esters, basestocks blends and 5 of the 6 formulated oils, the vapor pressure values calculated from the 6 1/2 hour test data is equal to or slightly greater than those values calculated from the 5% wt. loss data as required by ASTM Method D 2878. Factors contributing to this are the low and narrow volatility range of the lubricant components and the sample temperature being below test temperature during the first part of the test. Figure 1 shows the degree of linearity between evaporation and test time between 1 and 6 1/2 hours. Due to this and the standard specification test being 6 1/2 hours, evaporation values were conducted at temperatures ranging from 350°F to 415°F under standard air flow and test time. As shown by Figure 2, a linear relationship exists between the log of the evaporation value and reciprocal of temperature up to about 400°F. Above 400°F the rate of change in the evaporation decreases with increase in temperature and is probably due more to sample temperature lagging the bath temperature than lubricant composition change. Figure 3 shows that the evaporation values are not very sensitive to changes in air flow rates. For the formulated lubricants, the use of nitrogen in place of air changed the evaporation values only slightly. For the esters, use of nitrogen gave slightly lower evaporation values along with a noticeable decrease in lubricant degradation as shown by the total acid members obtained on the remaining sample after test. Formulated lubricants showed very little degradation during the test. The relationship between vapor pressure and temperature is given by Figure 4 and as would be expected from the weight loss versus temperature curves, vapor pressure values above 400°F are low compared to the values obtained up to 400°F.

Molecular weights of the formulated lubricants, basestocks and known esters were calculated from the 400°F evaporation data using ASTM D2787 as given in Table V. These values are all low by an average of about 52 molecular weight units. The expression $\log p = 2.48318 - 0.00539M$ was obtained from the vapor pressure and molecular weight data of the known esters as shown by Figure 5. The calculated molecular weights of the formulated lubricants and basestock ester blends when using this equation are given in Table VI. Average variation of these values with the theoretical values is about 24 molecular weight units. Molecular weights of the lubricants were calculated from the same expression, but using 6 1/2 hour evaporation data instead of the 5% wt. evaporation data. Average variation of these values is 29 molecular weight units and only slightly greater than that obtained from the 5% wt. evaporation data.



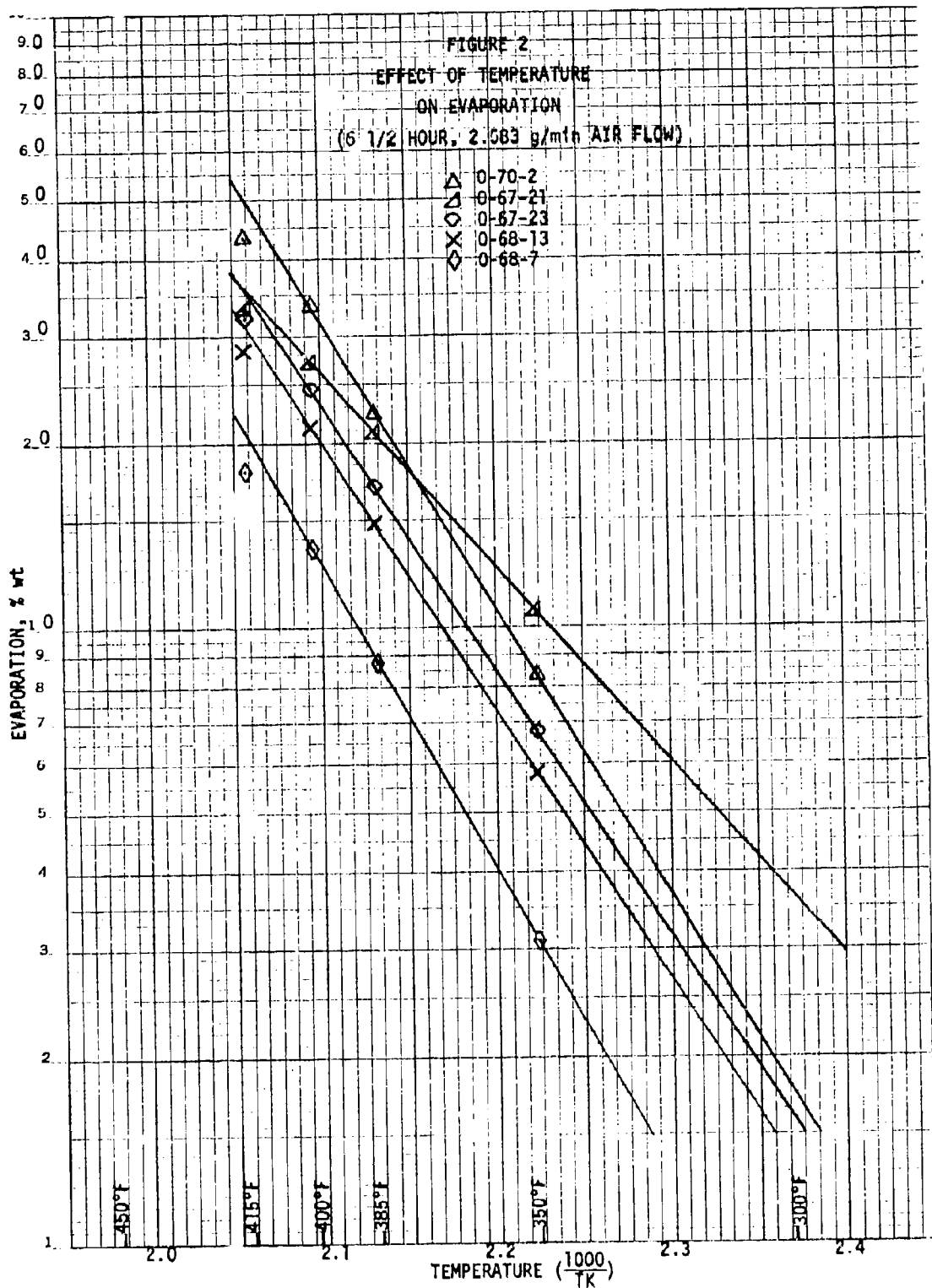
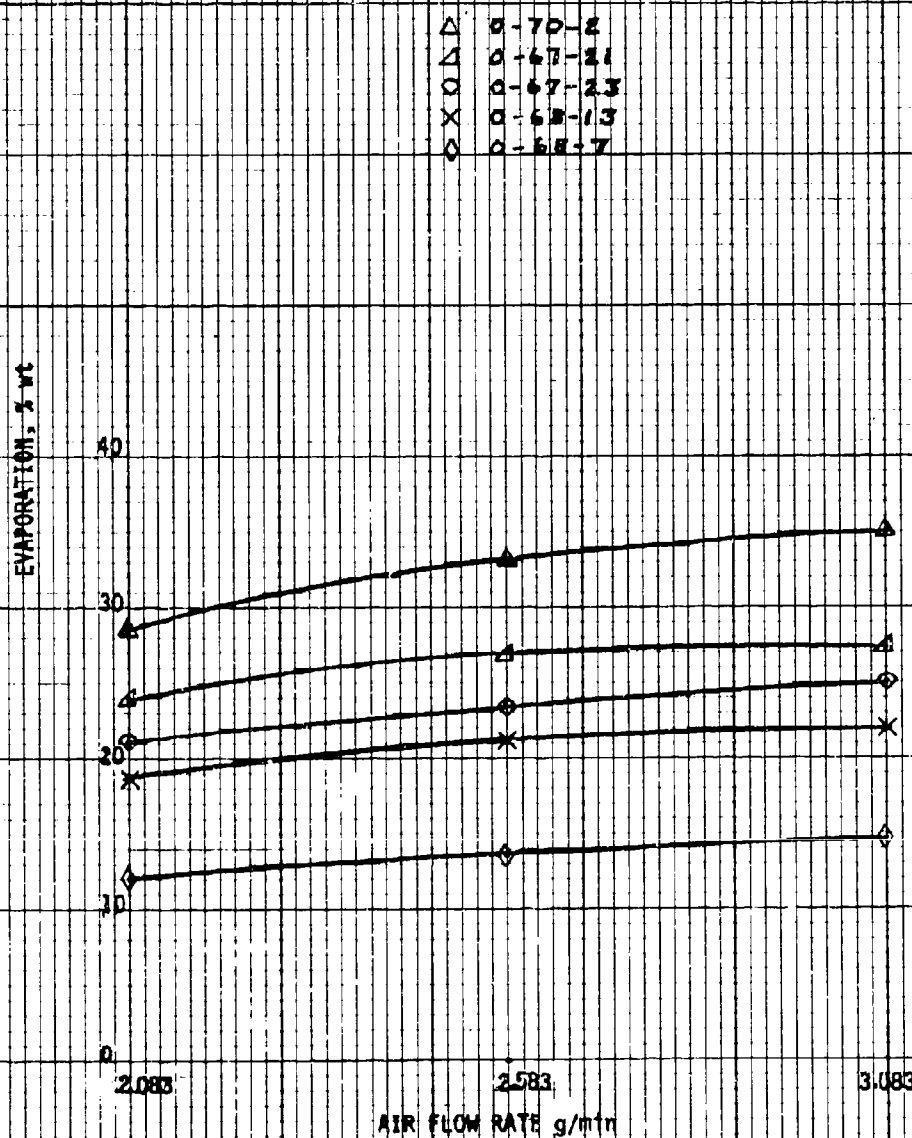
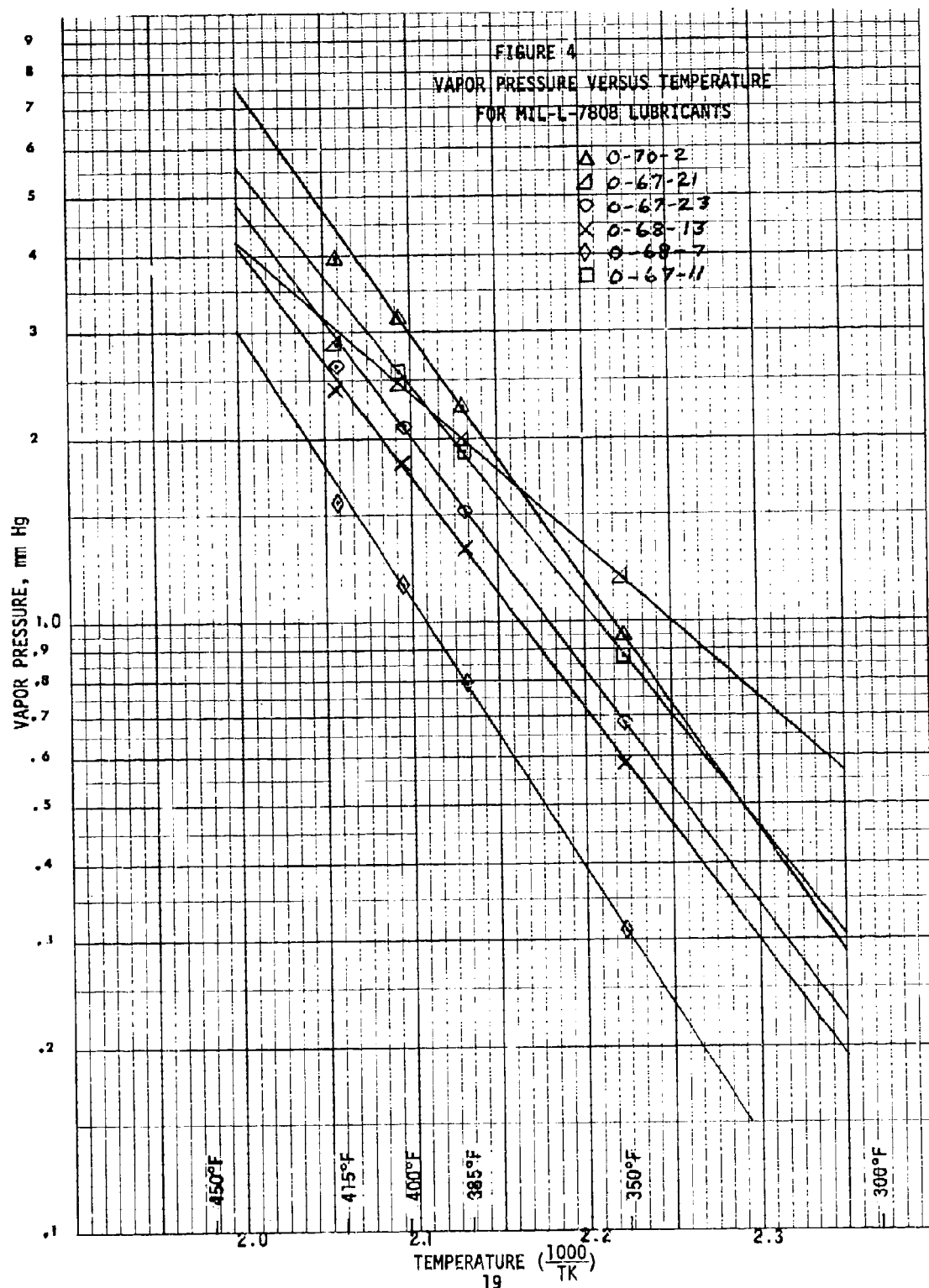
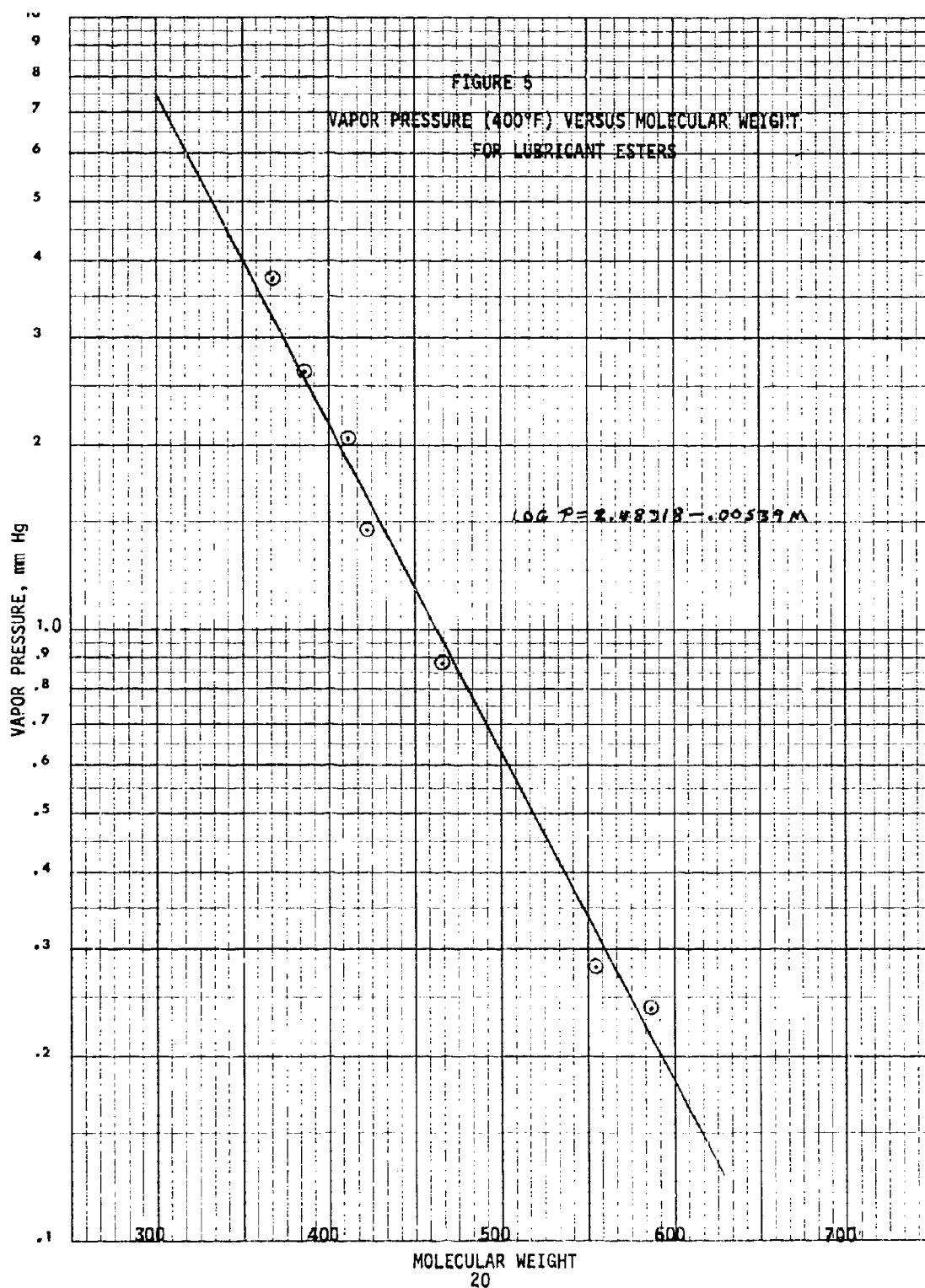


FIGURE 3
EFFECT OF AIR FLOW ON
EVAPORATION
(400°F, 6 1/2 HOUR TEST)







D. Thermogravimetric Analysis (TGA)

Thermogravimetric analyses of selected formulated lubricants were conducted to determine the suitability of the technique for measuring lubricant volatility, as described in Sections I and II.

Since the TGA weight loss-time (temperature) plot, either isothermal or temperature programmed, may be related to the volatility characteristics of a fluid, data were collected in both modes.

The results in the isothermal mode were disappointing because repeatability was poor. However, selected isothermal TGA 0-68-7 data were used to calculate and compare the volatilization energies of that lubricant as obtained by different methods. Results for other lubricants are not reported due to repeatability problems.

Due to problems encountered in previous attempts to instrumentally program the TGA oven to the desired temperature and hold that temperature precisely, the oven temperature was controlled manually. Because of the thermal mass of the oven and sample holder, that operation proved difficult. Major differences in volatilization rates were easily observable, e.g., the slow rate for 0-68-7 as compared to 0-70-2. The order for a series of lubricant evaporation rates typically agreed with D972 data, but with an estimated repeatability in the worst case of ± 0.5 mg/min, often data were overlapping to such an extent that comparisons were difficult. Without doubt, with more experimentation and refinement of technique, the precision of the method could be improved.

However, a more fruitful approach using available resources was thought to be the determination of lubricant evaporative characteristics by employing programmed temperature TGA. One difficulty associated with the TGA programmed temperature mode is data reduction. Because simple data reduction methods such as onset temperature are not satisfactory (Ref 8), one must resort to more tedious analytical methods than would be necessary if employing isothermal TGA or ASTM D972.

In order to reduce and compare data generated by the various test methods, a kinetic approach was selected where the apparent activation energy (E_A) was determined in each case. E_A may be thought of as the energy barrier which must be surmounted for a process to proceed. The E_A should be comparable irrespective of the test method employed to determine the value.

For an isothermal process such as ASTM D972, or isothermal TGA where the rate of evaporation is constant, E_A is easily obtained by plotting the log of rate data at several temperatures vs. the reciprocal of absolute temperature and then calculating the slope of the resulting data line (Ref 9) by use of the Arrhenius relationship:

$$\ln k = \ln Z - \frac{E_A}{RT}$$

where

k = rate constant

Z = pre-exponential factor (constant)

E_A = apparent activation energy (cal/mole)

R = gas constant (cal/deg mole)

T = absolute temperature (°K)

To predict evaporative rates at other temperatures in the same experimental confines and where the loss processes are known to be identical, Z must also be determined.

For programmed temperatures TGA, the method developed by Freeman and Carroll (Ref 10) was used to calculate E_A. The relationship derived is as follows:

$$\frac{\Delta \ln (-dw/dT)}{\Delta \ln (w_f - w)} = \frac{-E_A}{R} \frac{\Delta (1/T)}{\Delta \ln (w_f - w)} + n$$

where w = weight loss at any temperature (mg)

w_f = final weight loss (mg)

T = temperature (°K)

R = gas constant (cal/deg mole)

n = order of reaction

E_A = activation energy (cal/mole)

so that when $\frac{\Delta \ln (-dw/dT)}{\Delta \ln (w_f - w)}$ is plotted

vs. $\frac{\Delta (1/T)}{\Delta \ln (w_f - w)}$, as obtained from the thermogram, E_A may be

determined from the slope of the data line. If the data are from the earlier portions of the trace, E_A for the predominate evaporative process is obtained while data collected at higher temperatures shall typically reflect a combination of processes including oxidative and thermal degradation.

TGA data from the initial loss portions (~0-20 wt %) of five formulated lubricants were evaluated. Those data are given along with values calculated from loss rates obtained in ASTM D972 (385 and 400°F) in Table (7). The percent weight loss data for 400°F, 6.5 hour ASTM D972 tests are included.

TABLE VII
Lubricant Activation Energies and Weight Losses

Lubricant	TGA E_A (kcal/mole)	ASTM D972 E_A (kcal/mole)	ASTM D972 (400°F, 6.5 hr) % wt loss
0-67-21	15.7	14.9	27.0
0-67-23	18.2	19.8	24.5
0-68-7	24.9	25.0	13.5
0-68-13	19.9	21.3	21.3
0-70-2	16.6	18.3	33.2

Also, 210, 225 and 250°C 0-68-7 isothermal TGA data indicated an E_A of 24.3 kcal/mole, which is quite similar to values obtained using other test methods.

As stated previously, higher E_A 's are typically associated with lower rate constants; however, that simple correlation was not found in above data. The often overlooked influence of the pre-exponential factor was evidently very significant and shall be discussed in later sections.

Activation energies for D972 test data were easily calculated and confidently reported. However, because TGA values were for single runs only and many slope measurements were required for data reduction, the comparable E_A 's obtained by the different processes may have been fortuitous.

ASTM D972 415°F data were not used in the calculation. As the D972 test temperature was increased, the loss rate was found to be slightly less than predicted by the Arrhenius relationship from lower test temperature data. The minor deviation was probably due to slightly lower true sample temperatures.

Similar activation energies calculated for samples evaluated by all methods indicated comparable initial loss mechanisms. Also, within the test temperature ranges investigated, evaporation was the significant loss process. Tests under nitrogen supported that conclusion. The precision of calculated activation energies is estimated to be ± 2 kcal/mole. Again, for the majority of lubricants evaluated in a very limited number of tests, the energies calculated are comparable when obtained by either TGA or D972.

Perhaps the most significant point concerning activation energy data is that the values are derived from the slopes of reaction rate data and may be employed cautiously to propose process mechanisms. However, the data are subject to misinterpretation, especially the influence of the pre-exponential factor. Although the numerical value is trivial for these tests, the importance of the factor is readily apparent in Arrhenius plots; e.g., a low E_A was obtained for 0-67-21 (~15kcal/mole) as compared to

O-67-23 (~19kcal/mole), indicating that the evaporation rate for O-67-21 was less sensitive to temperature change than was O-67-23. However, the 6.5 hour D972 data were quite similar in the 385° - 415°F range, indicating large differences in Z. Again, the illustration indicates the need for caution when interpreting and comparing TGA and D972 data.

CONCLUSIONS AND RECOMMENDATIONS

A. ASTM Test Method D972.

The volatility characteristics of MIL-L-7808 lubricants can be accurately measured and controlled by ASTM Test Method D972 provided proper attention is given to test equipment and procedure used. ASTM Method D972 should require that evaporation test assemblies be checked with a standard material such as m-terphenyl and require evaporation values within specified limits. These limits should include testing at 400°F and 6 1/2 hours test time. Batch-to-batch variation in evaporation does not exist to the extent shown by current quality control testing. Use of a standard test material in ASTM D972 should reduce this variation. If not, a specification requirement for production lots to be within specified limits established from qualification data should be considered. Improved evaporation test repeatability can also be obtained through not interchanging test cell components once they have been checked through the use of a calibration standard such as m-terphenyl.

B. ASTM D-2878 Volatility Test Data. ASTM Method D-2878 provides a realistic and repeatable method for determining the vapor pressure of turbine lubricants in comparison to other techniques such as the isoteniscopes. Accuracy of this method is very much dependent upon the determination of the cell constant at different temperatures and the values of the vapor pressure of the M-terphenyl at these temperatures. ASTM D2878 should provide an

expression relating the vapor pressure of the m-terphenyl to temperature which would assist other laboratories in developing cell constants. The apparent molecular weight of formulated lubricants calculated from evaporation data agree quite well when one considers the purity of the commercial esters used for establishing the relationship of vapor pressure and molecular weight and in some cases may be more realistic than the calculated theoretical values based upon 100% pure esters.

C. Thermogravimetric Analysis (TGA).

Due to the necessity for numerous slope measurements and calculations required to reduce TGA data, the technique is best reserved in evaporation studies to those special cases, e.g., a small sample, where D972 data cannot be obtained. As stated earlier, activation energy data may be calculated; however, additional factors limit the usefulness of the values.

It is recommended that the ASTM D972 test be employed routinely for lubricant evaporation studies. The ease of data reduction and interpretation are factors which result in the choice of D972 over TGA for specification testing.

VI
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APPENDIX A
EVAPORATION TEST DATA

OIL CODE	TEST TEMP. °F	AIR FLOW g/min	N ₂ FLOW g/min	TEST TIME minutes	EVAPOR- ATION % wt	TOTAL ACID NUMBER
0-67-11	350°F	2.583		390	8.4	
	350°F	2.583		390	8.8	
	385°F	2.583		390	20.9	
	385°F	2.583		390	20.9	
	400°F	2.583		60	4.0	0.1
	400°F	2.583		60	4.2	
	400°F	2.583		390	29.2	
	400°F	2.583		390	30.2	
0-67-21	350	2.583		390	10.8	
	350	2.583		390	11.5	
	385	2.583		390	20.4	0.1
	385	2.583		390	21.4	
	385		2.583	390	20.1	0.1
	400	2.083		390	23.3	0.1
	400	2.083		390	24.8	
	400	2.583		50	4.0	0.1
	400	2.583		50	4.2	0.1
	400	2.583		60	5.4	0.1
	400	2.583		60	5.5	0.1
	400	2.583		60	5.6	0.1
	400	2.583		60	5.7	0.1
	400	2.583		80	7.3	0.1
	400	2.583		120	11.6	0.1
	400	2.583		120	12.0	0.1
	400	2.583		240	18.1	0.1
	400	2.583		240	19.5	
	400	2.583		390	27.8	
	400	2.583		390	27.6	
	400	2.583		390	25.7	0.2
	400		2.583	390	25.7	0.1
	400	3.083		390	26.7	0.1
	400	3.083		390	28.0	
	415	2.583		390	32.1	0.1
	415	2.583		390	33.7	
	415		2.583	390	32.3	0.1
B-67-21 Basestock	400	2.583		60	5.7	0.5
	400	2.583		60	6.0	
	400	2.583		60	5.5	0.3
	400	2.583		390	29.8	3.8
	400	2.583		390	31.1	
0-67-23	350	2.583		390	6.6	
	350	2.583		390	7.0	
	385	2.583		390	16.5	0.1
	385	2.583		390	17.6	
	385		2.583	390	17.4	0.0
	400	2.083		390	20.3	0.3
	400	2.083		390	21.9	
	400	2.583		60	3.4	0.1
	400	2.583		60	3.5	

APPENDIX A
EVAPORATION TEST DATA (CONT)

OIL CODE	TEST TEMP °F	AIR FLOW g/min	N ₂ FLOW g/min	TEST TIME minutes	EVAPOR-ATION % wt	TOTAL ACID NUMBER
0-67-23 (Cont)	400	2.583		80	4.8	
	400	2.583		120	7.1	0.1
	400	2.583		120	7.5	
	400	2.583		390	23.6	0.1
	400	2.583		390	23.8	
	400	2.583		390	26.2	
	400		2.583	390	23.2	0.1
	400	3.083		390	24.7	0.2
	400	3.083		390	25.6	
	415	2.583		390	30.8	
	415	2.583		390	33.2	0.6
	415		2.583	390	31.8	0.1
	400	2.583		80	4.3	0.4
	400	2.583		80	4.6	
B-67-23 Basestock	400	2.583		390	25.9	3.5
	400	2.583		390	27.4	
0-68-7	350	2.583		390	3.0	0.2
	350	2.583		390	3.2	
	385	2.583		390	8.4	0.3
	385	2.583		390	9.1	
	385		2.583	390	8.1	0.1
	400	2.038		390	11.6	0.5
	400	2.038		390	12.6	
	400	2.583		60	1.7	0.2
	400	2.583		60	1.8	
	400	2.583		120	3.9	0.2
	400	2.583		120	4.0	
	400	2.583		150	4.4	
	400	2.583		150	4.7	
	400	2.583		390	13.9	
	400	2.583		390	12.0	0.2
	400	2.583		390	14.6	
	400			390	11.8	0.1
	400	3.083		390	12.4	0.5
	400	3.083		390	13.8	
	400	3.083		390	13.2	
	400	3.083		390	14.2	0.5
	415	2.583		390	17.9	1.1
	415	2.583		390	20.4	
	415		2.583	390	18.9	0.1
B-68-7 Basestock	400	2.583		150	4.8	0.8
	400	2.583		150	5.7	
	400	2.583		390	19.9	5.1
	400	2.583		390	20.4	
0-68-13	350	2.583		390	5.8	
	385	2.583		390	14.2	0.2
	385	2.583		390	15.4	
	385		2.583	390	14.4	0.1
	400	2.083		390	17.9	0.3
	400	2.083		390	19.2	

APPENDIX A
EVAPORATION TEST DATA

OIL CODE	TEST TEMP °F	AIR FLOW g/min	N ₂ FLOW g/min	TEST TIME minutes	EVAPOR- ATION % wt	TOTAL ACID NUMBER
0-68-13 (Cont)	400	2.583		60	2.9	
	400	2.583		60	3.1	
	400	2.583		90	4.8	0.1
	400	2.583		90	5.3	
	400	2.583		90	4.5	
	400	2.583		120	7.0	0.3
	400	2.583		120	5.7	
	400	2.583		390	20.1	
	400	2.583		390	19.8	
	400	2.583		390	21.0	
	400	2.583		390	21.7	
	400	2.583		390	21.0	
	400	2.583		390	21.9	
	400	2.583		390	22.2	
	400	2.583		390	22.9	
	400	2.583		390	20.9	
	400	2.583		390	20.7	0.1
	400	*2.583		390	19.5	0.4
	400	*2.583		390	20.9	0.3
	400		2.583	390	20.2	0.1
	400	3.083		390	22.7	
	415	2.583		390	27.7	0.3
	415	2.583		390	29.5	
	415		2.583	390	28.7	0.1
B-68-13 Basestock	400	2.583		80	3.8	0.3
	400	2.583		80	3.9	
	400	2.583		390	25.0	3.9
	400	2.583		390	26.1	
0-70-2	350	2.583		390	8.4	
	385	2.583		390	21.6	0.8
	385	2.583		390	23.3	
	385		2.583	390	20.9	0.2
	400	2.083		390	27.4	0.9
	400	2.083		390	29.2	
	400	2.583		60	4.2	0.3
	400	2.583		60	4.2	
	400	2.583		60	4.7	
	400	2.583		120	9.7	0.4
	400	2.583		120	10.4	
	400	2.583		150	12.7	
	400	2.583		150	13.3	
	400	2.583		240	21.1	
	400	2.583		240	22.2	
	400	2.583		390	31.8	0.6
	400	2.583		390	34.7	
	400		2.583	390	30.2	0.2
	400	3.083		390	34.3	0.9
	400	3.083		390	36.1	
	415	2.583		390	43.4	1.4
	415		2.583	390	41.9	

*Wet Air

APPENDIX A
EVAPORATION TEST DATA

OIL CODE	TEST TEMP °F	AIR FLOW g/min	N ₂ FLOW g/min	TEST TIME minutes	EVAPORATION % wt	TOTAL ACID NUMBER
B-70-2 Basestock	400	2.583		60	4.8	0.9
	400	2.583		60	5.2	
	400	2.583		60	4.6	0.7
	400	2.583		390	38.0	8.3
	400	2.583		390	40.8	
O-71-6	400	2.583		390	5.3	
	400	2.583		390	5.9	
E-105	400	2.583		60	5.5	0.8
	400	2.583		60	5.9	
	400		2.583	60	5.4	0.1
	400		2.583	60	5.9	
E-109	400	2.583		80	4.3	
	400	2.583		80	4.6	
	400	2.583		120	6.1	0.6
	400	2.583		390	22.4	6.8
	400	2.583		390	22.7	
	400		2.583	120	5.1	0.1
	400		2.583	120	5.9	
E-120	400	2.583		60	4.0	0.4
	400	2.583		60	4.3	
	400		2.583	60	4.6	0.0
	400		2.583	60	4.6	
	400		2.583	120	10.8	
	400		2.583	120	11.6	
E-129	400	2.583		195	4.4	
	400	2.583		195	4.7	
	400	2.583		390	12.0	
	400	2.583		390	11.4	
	400	2.583		390	10.1	2.43
	400	2.583		390	10.4	
	400		2.583	240	4.9	
	400		2.583	240	5.4	
E-139	400	2.583		120	5.4	0.6
	400	2.583		120	4.8	
	400	2.583		210	10.5	
	400	2.583		210	11.0	
	400	2.583		210	9.6	
	400	2.583		210	9.9	
	400		2.583	120	3.0	0.1
	400		2.583	120	3.1	
E-149	400	2.583		390	3.7	
	400	2.583		390	4.0	
	400		2.583	390	1.2	
	400		2.583	390	1.2	
	400		2.583	390	1.1	0.0
	400		2.583	390	1.2	
E-159	400	2.583		60	0.56	0.4
	400	2.583		60	0.56	
	400	2.583		390	4.2	
	400	2.583		390	4.2	
	400		2.583	390	1.8	0.1
	400		2.583	390	1.9	

APPENDIX A
EVAPORATION TEST DATA

OIL CODE	TEST TEMP °F	AIR FLOW g/min	N ₂ FLOW g/min	TEST TIME minutes	EVAPORATION % wt	TOTAL ACID NUMBER
LUBRICANT A, LOT A	400	2.583		390	24.2	0.5
	400	2.583		390	26.4	0.4
LOT A-1	400	2.583		390	25.3	
	400	2.583		390	24.6	
LOT A-2	400	2.583		390	24.4	
	400	2.583		390	26.6	0.5
LOT A-3	400	2.583		390	26.6	
	400	2.583		390	25.7	
	400	2.583		390	24.6	
	400	2.583		390	24.3	
	400	2.583		390	24.6	
	400	2.583		390	26.6	
LOT A-3 CUP & CELL COVER REVERSED	400	2.583		390	25.1	
	400	2.583		390	25.4	
	400	2.583		390	25.0	
	400	2.583		390	25.2	
	400	2.583		390	25.3	
	400	2.583		390	25.3	
LOT A-3 CUP REVERSE	400	2.583		390	26.6	
	400	2.583		390	26.5	
					25.3	
					25.3	
LOT A-3 CELL COVER REV.	400	2.583		390	25.4	
	400	2.583		390	25.0	
	400	2.583		390	25.3	
	400	2.583		390	25.3	
LUBRICANT B LOT B	400	2.583		390	14.7	0.3
	400	2.583		390	15.6	
LOT B-1	400	2.583		390	15.7	0.2
	400	2.583		390	14.5	
LOT B-2	400	2.583		390	14.9	0.3
	400	2.583		390	15.6	
LUBRICANT C LOT C	400	2.583		390	34.2	0.7
	400	2.583		390	36.8	
LOT C-1	400	2.583		390	35.8	0.6
	400	2.583		390	33.8	
LOT C-2	400	2.583		390	34.9	

APPENDIX A
EVAPORATION TEST DATA

OIL CODE	TEST TEMP °F	AIR FLOW g/min	N ₂ FLOW g/min	TEST TIME minutes	EVAPOR- ATION % wt	TOTAL ACID NUMBER
m-TERPHENYL	250	2.583		1320	2.91	
	300	2.583		390	4.67	
	300	2.583		390	5.06	
	300	2.583		390	4.87	
	300	2.583		390	5.13	
	300		2.583	390	4.87	
	300		2.583	390	5.13	
	400	2.583		390	66.3	
	400	2.583		390	67.2	
	400	2.583		390	66.5	
	400	2.583		390	68.4	
	400	2.583		390	67.4	
	400	2.583		390	65.4	